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(54) Title: MATERIAL FOR ABSORBING AQUEOUS FLUIDS

(57) Abstract

Water absorbent compositions comprise a water swellable polymer which contains polymerized water-soluble monomers, water-insoluble monomers having a pendant hydrophobic moiety, and optionally, a cross-linking monomer. The polymer can be blended with a colloidal support such as colloidal silica. The compositions exhibit good water absorbency rates and high gel strengths.

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MATERIAL FOR ABSORBING AQUEOUS FLUIDS

The present invention relates to water-swellable polymers which are useful in absorbing aqueous fluids.

Water absorbent materials comprising water-swellable polymers have provided various uses in the art. See, for example, U.S. Patent Nos. 3,926,891; 4,190,562; 4,293,609 and 4,424,247. Numerous disposable articles containing such water-swellable polymers are disclosed as in U.S. Patent Nos. 3,669,103 and 3,888,257.

Water-swellable polymers which are useful in providing absorbent materials are typically polymers comprising crosslinked acrylamide; hydrolyzed acrylamide; acrylic acid; hydrolyzed acrylates; hydrolyzed acrylonitrile; and grafted starch and celluloses; and the like.

Such polymers require considerable care in controlling the amount of crosslinking which is present. For example, if the amount of crosslinking in the polymer is increased, the gel strength of the resulting polymer network is increased at the expense of reducing the capacity of the gel to absorb fluid. On the other hand,

at low degrees of crosslinking the gels have a poor, slimy consistency which exhibit low gel strengths.

In view of the fact that the utility of known water-absorbent materials is limited due to lack of 5 integrity of the gel structure during use, insufficient absorbing capacity and absorbing rate, and difficulties in crosslinking the polymers which are employed; it would be highly desirable to provide a novel, highly absorbent polymer system having a high gel strength and 10 minimal amounts of crosslinking.

The present invention is a composition capable of absorbing an aqueous liquid which composition comprises a functionally effective amount of a swellable addition polymer comprising, in polymerized form, (a) a 15 major portion of at least one water-soluble monomer, (b) a minor portion of at least one water-insoluble monomer having a pendant hydrophobic moiety and, optionally, (c) a minor portion of a crosslinkable monomer in an amount sufficient to provide gel strength to the 20 polymer; which polymer is polymerized in the presence of at least a micelle forming amount of a surfactant composition containing at least one ionic surfactant; and which polymer is capable of undergoing hydrophobic 25 association through hydrophobic groups of said polymer such that said polymer is swellable but not readily soluble in the presence of an aqueous liquid when said polymer is in intimate contact with an amount of surfactant, if any, which is less than that amount of surfactant which will solubilize said polymer in said aqueous 30 liquid.

The composition of the present invention may additionally contain a functionally effective amount of an inorganic colloidal support.

The compositions of this invention, which 5 have absorbed aqueous fluids, exhibit gel strengths which can increase with time. That is, swollen gel particles of this invention in contact with one another are capable of forming one large continuous gel particle by what is believed to be intergel associations. This 10 expected change in structure of the gel provides an increase in gel strength of the gel as a whole. In addition, the formation of a large gel particle provides a gel having less tendency to migrate during use. Gels of this invention have improved adhesive and elasticity 15 characteristics.

The compositions of this invention are capable of absorbing many times their own weight of an aqueous fluid. That is, the compositions of this invention can have improved aqueous fluid absorbing capacity, exhibit 20 improved rates of aqueous fluid absorption, and have improved gel strengths. Consequently, the compositions are useful in providing a process for absorbing large amounts of an aqueous fluid. The compositions are useful in a wide variety of applications wherein water- 25 absorbent polymeric materials have been used.

By "hydrophobic associative" is meant that, in aqueous media, the pendant hydrophobic moieties of the polymer associate thereby preventing solubilization

and providing swellability of the polymer in an aqueous medium.

The hydrophilic/hydrophobic polymer (i.e., water swellable addition polymer) is predominantly hydrophilic, 5 but contains a sufficient concentration of suitable hydrophobic moieties to enable it to associate with other hydrophobic moieties and the hydrophobic moieties of any surfactant which is present to cause a substantial swellability of the polymer in the presence of an 10 aqueous medium. That is, the hydrophilic monomers polymerize to form a major portion of the polymer and the hydrophobic monomers polymerize to form a minor portion of the polymer. The polymer has an unassociated molecular weight which can vary such that the polymer 15 will form a gel. Polymers having very high molecular weight, e.g., weight average molecular weight greater than 5 million, are believed to be suitably employed. Preferably, the hydrophilic/hydrophobic polymers used in this invention have weight average molecular weights 20 in the range from 200,000 to 10 million, most preferably from 800,000 to 5 million. See U.S. Patent No. 4,432,881.

The hydrophobic groups of the hydrophilic/hydrophobic polymer are preferably pendant organic groups having hydrophobicities comparable to one of the following: 25 aliphatic hydrocarbon groups having at least four carbons atoms such as C₄ to C₂₀ alkyls and cycloalkyls; aromatic and aromatic hydrocarbon groups such as naphthyls; alkylaryls wherein alkyl has one or more carbon atoms, preferably 4 to 8 carbon atoms; haloalkyls of 4 or more 30 carbon atoms, preferably perfluoroalkyls; polyalkyleneoxy

groups wherein alkylene is propylene or higher alkylene and there is at least 1 alkyleneoxy unit per hydrophobic moiety.

Suitable hydrophobic monomers include those

5 which are (1) water-insoluble, i.e., where less than 0.4, preferably less than 0.2, weight part of the hydrophobic monomer will dissolve in 100 weight parts water and (2) ethylenically unsaturated compounds having hydrophobic groups as defined hereinbefore. Exemplary hydrophobic

10 monomers include the higher alkyl esters of α,β -ethylenically unsaturated carboxylic acids such as dodecyl acrylate, dodecyl methacrylate, tridecyl acrylate, tridecyl methacrylate, tetradecyl acrylate, tetradecyl methacrylate, octadecyl acrylate, octadecyl methacrylate, ethyl half

15 ester of maleic anhydride, diethyl maleate, and other alkyl esters derived from the reactions of alkanols having from 4 to 20, preferably from 8 to 20, carbon atoms with ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, fumaric acid, itaconic acid and aconitic acid, and maleic anhydride; 20 alkylaryl esters of ethylenically unsaturated carboxylic acids such as nonyl- α -phenyl acrylate, nonyl- α -phenyl methacrylate, dodecyl- α -phenyl acrylate and dodecyl- α -phenyl methacrylate; N-alkyl ethylenically unsaturated

25 amides such as N-octadecyl acrylamide, N-octadecyl methacrylamide, N,N-dioctyl acrylamide and similar derivatives thereof; α -olefins such as octene-1-, decene-1, dodecene-1 and hexadecene-1; vinyl alkylates wherein alkyl has at least 8 carbons such as vinyl

30 laurate and vinyl stearate; vinyl alkyl ethers such as dodecyl vinyl ether and hexadecyl vinyl ether; N-vinyl amides such as N-vinyl lauramide and N-vinyl stearamide; and ar-alkylstyrenes such as t-butyl styrene. Of the foregoing hydrophobic monomers, the alkyl ester of

acrylic acid, methacrylic acid, N-alkyl acrylamides and N-alkyl methacrylamides wherein alkyl has from 8 to 20 carbon atoms, styrene and the alkyl styrenes wherein alkyl has from 4 to 8 carbons such as t-butyl, are 5 preferred. The alkylmethacrylates and alkylacrylates wherein alkyl has from 10 to 20 carbon atoms are more preferred. Dodecyl methacrylate and N-dodecyl methacrylamide are the most preferred where hydrolysis is not a problem.

Suitable water-soluble monomers include those 10 ionizable or hydrolyzable monomers which are sufficiently water-soluble to form at least a 10 weight percent solution when dissolved in water and readily undergo addition polymerization to form polymers which are water-soluble. Exemplary water-soluble monomers include 15 ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, itaconic acid and fumaric acid; ethylenically unsaturated amides such as acrylamide, methacrylamide and fumaramide and their N-substituted derivatives such as 2-acrylamido-2-methylpropane 20 sulfonic acid (AMPS), N-(dimethylaminomethyl)acrylamide as well as N-(trimethylammoniummethyl)acrylamide chloride and N-(trimethylammoniumpropyl)methacrylamide chloride; and other ethylenically unsaturated quaternary ammonium compounds such as vinylbenzyl trimethyl ammonium chloride; 25 sulfoalkyl esters of unsaturated carboxylic acids such as 2-sulfoethyl methacrylate, aminoalkyl esters of unsaturated carboxylic acids such as 2-aminoethyl methacrylate; vinyl amines such as vinyl pyridine and vinyl morpholine; diallyl amines and diallyl ammonium 30 compounds such as diallyl dimethyl ammonium chloride, vinyl heterocyclic amides such as vinyl pyrrolidone,

vinylaryl sulfonates such as vinylbenzyl sulfonate; as well as the salts of the foregoing monomers. Preferable salts include the sodium, potassium and ammonium salts of the monomers. Of the foregoing water-soluble monomers, 5 acrylic acid, including salts of acrylic acid such as sodium acrylate or ammonium acrylate, and acrylamide and combinations of these are preferred. Hydrolyzable monomers can also be employed.

The hydrophilic/hydrophobic polymer is preferably an addition copolymer of a water-soluble ethylenically unsaturated monomer and an ethylenically unsaturated monomer having sufficient concentration of hydrophobic groups to enable the resulting polymer to form a gel under conditions of use. Exemplary preferred polymers 10 include copolymers of from 90 to 99.995, more preferably from 98 to 99.995, most preferably from 99 to 99.9, mole percent of one or more water-soluble monomers with from 0.005 to 10, more preferably from 0.005 to 2, most preferably from 0.1 to 1, mole percent of one or more 15 hydrophobic monomers. For these polymers, preferred amounts of hydrophobic monomers can vary with the 20 molecular weight of the polymer.

The crosslinking of the monomers can be provided by a variety of means. See, for example, U.S. 25 Patent No. 4,293,609. The amount of crosslinking agent can vary and can suitably range from 0 to 5 weight percent, preferably from 300 to 3,000 ppm of crosslinkable monomer, based on all polymerized monomers. Preferably, the crosslinking agent is a polyvinyl monomer. Examples 30 of polyvinyl monomers include divinyl benzene, acryloyl or methacrylyl polyesters of polyhydroxylated compounds,

divinyl esters of polycarboxylic acid, diallyl esters of polycarboxylic acids, diallyl dimethyl ammonium chloride, triallyl terephthalate, methylene bisacrylamide, diallyl maleate, diallyl fumarate, hexamethylene bis 5 maleimide, triallyl phosphate, trivinyl trimellitate, divinyl adipate, glyceryl trimethacrylate, diallyl succinate, divinyl ether, the divinyl ethers of ethylene glycol or diethylene glycol diacrylate, polyethylene glycol diacrylates or methacrylates, 1,6-hexanediol 10 diacrylate, pentaerythritol triacrylate or tetracrylate, neopentyl glycol diacrylate, cyclopentadiene diacrylate, the butylene glycol diacrylates or dimethylacrylates, and trimethylolpropane di- or tri-acrylates.

15 The polymers of this invention can be prepared using aqueous solution techniques, inverse bead suspension techniques, spray bead polymerization techniques using UV catalysis, or other such techniques. Preferred methods of preparation include the aqueous solution techniques.

20 The aforementioned hydrophilic/hydrophobic polymers containing hydrophobic moieties are advantageously prepared by copolymerizing the water-soluble monomers with hydrophobic monomers in an aqueous medium containing an ionic surfactant or emulsifier that 25 solubilizes the hydrophobic monomer in the aqueous medium. By solubilizing the hydrophobic monomer in the aqueous medium, the combination of aqueous medium, hydrophobic monomer and surfactant gives the visual appearance of a clear or translucent solution. That 30 is, a micelle forming amount of a surfactant is employed. This copolymerization is preferably accomplished.

in an aqueous medium containing a polymerization initiator capable of generating free-radicals. Optionally, a chain transfer agent may be included in the polymerization reaction mixture.

5 The solubilizing surfactant is required in most instances to suitably solubilize the hydrophobic monomer and to subsequently obtain a hydrophilic/hydrophobic polymer having a desirable concentration of hydrophobic moieties in the polymer. It is believed
10 that the hydrophobic monomer is solubilized in the micelles formed by the surfactant. Thus, the surfactant is generally employed in an amount which is above the critical micelle concentration (CMC) of the surfactant or surfactant mixture, but less than that which reduces
15 the concentration of hydrophobic monomer in the resultant hydrophilic/hydrophobic polymer to a point that the polymer will not form a gel under the conditions in which the product is used. The amount of surfactant used will also be such that there is believed to be at
20 least one hydrophobic monomer molecule per micelle of the surfactant. An upper limit to the amount of hydrophobic monomer which is employed is based on that level which can be solubilized by the surfactant, i.e., an amount of hydrophobic monomer below which the reaction mixture
25 becomes cloudy. For example, when sodium dodecyl sulfate (NaDS) is employed as a surfactant for dodecyl methacrylate (DMA), the molar ratio of DMA to NaDS is from at least 1:50 up to 1:2, preferably from 1:5 to 1:25, most preferably from 1:10 to 1:15. By knowing
30 the CMC, the hydrophilic-lipophilic balances (HLB) and aggregation number of molecules in the micelle molecular weight of a surfactant and the hydrophobicity of the hydrophobic monomer, suitable molar ratios and appropriate

surfactant concentrations can be determined for any given hydrophobic monomer and surfactant to provide similar suitable concentrations of hydrophobic moieties in the hydrophilic/hydrophobic polymer.

5 Suitable surfactants include, for example, anionic agents such as alkali metal salts of alkyl sulfates and alkyl and aryl sulfonates, e.g., dodecyl alkyl sulfosuccinates and sodium dodecylbenzene sulfonate; fatty acid soaps, e.g., sodium oleate, sodium 10 stearate and potassium oleate; alkali metal salts of sulfonated fatty alcohols, e.g., sodium dodecyl sulfate; sulfates of ethoxylated alcohols; alkyl phosphate esters, e.g., dodecyl hydrogen phosphate; and fluoro emulsifiers, e.g., perfluoroalkyl sulfates. 15 Also included are cationic surfactants such as alkylamine hydrochlorides, e.g., dodecylamine hydrochloride and tridecylamine hydrochloride; quaternary alkyl or aryl ammonium halides such as dodecyl trimethyl ammonium chloride; ethoxylated fatty amines and other surfactant as described in 20 McCutcheon's Detergents and Emulsifiers, North American Edition, 1980 Annual. In general, when the hydrophilic/hydrophobic polymer is anionic or nonionic, an anionic surfactant such as an alkali metal alkyl sulfate is 25 preferably employed as the surfactant. When the hydrophilic/hydrophobic polymer is cationic, a cationic surfactant such as dodecylamine hydrochloride is preferably employed. When the hydrophilic/hydrophobic polymer is nonionic, anionic or cationic, a nonionic surfactant 30 such as nonylphenoxy polyethylene glycol having 10 ethyleneoxy units per molecule or other water-dispersible nonionic surfactants as defined herein can be employed subject to the condition that an ionic surfactant be employed.

Exemplary suitable polymerization initiators include the azo catalysts such as azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylpentanenitrile) and dimethyl azoisobutyrate; organic peroxygen compounds such as 5 benzoyl peroxide, t-butyl peroxide, diisopropyl benzene hydroperoxide and t-butyl hydroperoxide; and inorganic persulfates such as potassium persulfate, ammonium persulfate and sodium persulfate. Of these initiators, the oil-soluble types such as the organic peroxides and 10 azo compounds are preferred. It is desirable to employ from 0.01 to 0.1 weight percent of initiator based on the monomers.

In an optional embodiment, a nonionic surfactant is added to the polymerization recipe as another 15 component in addition to the ionic surfactant, i.e., emulsifier. Alternatively, it is suitable to add the nonionic surfactant to the hydrophilic/hydrophobic polymer subsequent to polymerization. Exemplary nonionic surfactants include the reaction products of ethylene 20 oxide or mixtures of ethylene oxide and higher alkylene oxide with active hydrogen compounds such as phenols, alcohols, carboxylic acids and amines, e.g., alkyl-phenoxyethyleneoxy ethanols. More preferred nonionic surfactants are the alkyl polyethyleneoxy compounds 25 represented by the formula:



wherein R is C_8-C_{18} alkyl, EO is ethyleneoxy and n is a number from 1 to 10. Other suitable nonionic surfactants are described in McCutcheon's, supra. Of the 30 foregoing surfactants, the ethoxylated alkyl phenol and ethoxylated fatty alcohols are more preferred.

Suitable anionic substituted polyethyleneoxy compounds useful herein are represented by the formula:



wherein R and n are as defined hereinbefore, EO is ethyleneoxy and X is SO_3H or CH_2CO_2H or PO_3H ; salts of long chain carboxylates such as, for example, potassium oleate, sodium laurate, potassium stearate, potassium caprolate, and sodium palmatate; alkali metal alkylbenzene sulfonates such as sodium nonylbenzene sulfonate and potassium dodecylbenzene sulfonate; alkali metal alkyl sulfates such as sodium dodecyl sulfate and alkali metal dialkyl sulfosuccinates such as sodium dihexyl sulfosuccinate and sodium dioctyl sulfosuccinate; salts of resin acids such as abietic acid and dihydroabietic acid..

The hydrophilic/hydrophobic polymers when made using unneutralized acidic monomers are conveniently neutralized using organic or inorganic bases, by mixing the polymer with the base. Bases such as, for example, ammonia, ammonium hydroxide, alkali metal hydroxides, alkali metal bicarbonates, carbonates, alkali metal salts of basic phosphates, silicates, organic amines such as alkyl amines, and alkanol amines can be used. It is also understood that the polymer can be neutralized after recovering the polymer, if so required. The degree of neutralization in the polymers can vary from 0 to 100 percent, preferably from 50 to 80 percent.

The hydrophilic/hydrophobic polymers are readily recovered from the aqueous medium when such is

desired by removal of water under vacuum or by azeotropic distillation or by drum drying. The polymer can be ground to the desired size (e.g., such as a powder, prior to use).

5 It is also understood that hydrophilic/hydrophobic polymers of monomers such as acrylamide or methylacrylate, acrylic acid and hydrophobic monomer can be prepared by copolymerizing all three of these monomers or by copolymerizing acrylamide or methyl-
10 acrylate with the hydrophobic monomer and subsequently hydrolyzing a portion of the copolymerized hydrolyzable monomer such as acrylamide or methylacrylate by contacting the copolymer with a base such as sodium hydroxide and/or sodium carbonate.

15 The inorganic colloidal support is preferably a water-insoluble material which has a particle size small enough that the particles disperse in an aqueous solution to yield transparent or translucent fluids. Typical colloidal particles which are useful as colloidal
20 supports are inorganic materials having a particle diameter from 50 Å to 200 Å (5 to 20 nm), preferably from 80 Å to 100 Å (8 to 10 nm). Clusters of particles are not generally larger than 1,000 Å (100 nm) in diameter. Colloidal supports can be made of any
25 substantially water-insoluble inorganic materials. Suitable materials include, for example, colloidal or fumed silica, alumina, and titania as well as colloidal oxide solutions such as those containing, for example, zinc, zirconium, nickel, iron, or cobalt.

30 The polymer can be blended with the colloidal support using a variety of techniques. For example, the support and polymer can be dry blended. Most

preferably, the support is dispersed in an aqueous liquid and contacted with the polymer, which is either in a gel or a dry state. The support and polymer mixture can be dried, if desired. It is also possible 5 to polymerize the monomers in the presence of a dispersed colloidal support.

The amount of colloidal support which is employed can vary. Suitable amounts of the colloidal support range from 0 to 80, preferably from 0.2 to 50, 10 weight percent based on the weight of polymer and support. Such compositions can exhibit increased gel strengths over those compositions not containing the colloidal support.

The compositions of this invention can be 15 further, though optionally, blended with a desired inorganic filler which can be non-colloidal in nature. Although the materials can be physically blended using a wide variety of means, dry blending is preferred. That is, an essentially dry polymer is physically mixed 20 with the desired filler which is an essentially dry inorganic powder. Thorough mixing insures good gel strength of the composition. Generally the order of addition of components is not particularly critical. More preferably, the filler is added to the components 25 present in the polymerization recipe before total polymerization has occurred.

By the term "filler" is meant a very finely divided water insoluble or sparingly water-soluble grouping or aggregate of solid particles, usually 30 smaller than 1,000 μm but which is not generally colloidal in nature. Inorganic powders especially

preferred herein include alumina trihydrate and a wide variety of clays. Specific examples include sodium bentonite (montmorillonite clay), kaolinite and attapulgite. Other inorganic powders include, for example, white 5 carbon, synthetic silicate white carbon, basic magnesium carbonate, ultrafine magnesium silicate, light or heavy calcium carbonate, soft or hard clays, talc, vermiculite, perlite, barium sulfate, and mica.

10 The amount of polymer and optional colloidal support employed in blends with filler can preferably range from 20 to 100, more preferably from 40 to 75, and most preferably from 60 to 70, weight percent of polymer and colloidal support based on the total weight of the polymer, colloidal support and filler. Conversely, 15 the amount of filler useful herein preferably ranges from 0 to 80, more preferably from 25 to 60, and most preferably from 30 to 40, weight percent of said filler based on the total weight of the polymer, colloidal support and filler.

20 Such blended compositions (i.e., containing polymer, optional colloidal support and filler) can exhibit further increased gel strengths over those compositions containing a polymer and not containing the inorganic filler. The high gel strengths of such 25 compositions allow for products exhibiting good utilization of water absorbent capacity as well as good integrity. In this regard, the compositions of this invention are easy to handle and can be employed in a wider variety of applications compared to previously 30 employed water absorbent materials.

The compositions of this invention can be incorporated into film laminates and other such materials as are described, for example, in U.S. Patent Nos. 4,117,184; 4,176,677; 4,293,609 and 4,424,247. For 5 example, polymer compositions can be incorporated in wicking substrates and treated as described in U.S. Patent No. 4,293,609. Such materials exhibit high water absorbent capabilities. The compositions of this invention and the laminates prepared therefrom can be 10 incorporated into absorbent devices. The compositions can be used in those applications which have employed hydrophilic polymers as highly absorbent materials. The compositions can be employed in conjunction with 15 water-absorbent polymeric materials known in the art, as for example, polymeric blends.

The compositions of this invention can be shaped and formed for use in a wide variety of applications. For example, the compositions can be formed into sheets, filaments, coatings or molded articles. 20 The compositions can be foamed, extruded into articles or extruded into a pellet form. The compositions of this invention can be incorporated into a wide variety of product forms.

25 Uses of the increased gel strength composition of the present invention include applications such as, for example, shut-off filters for fuels such as gasoline, oil, and hydraulic fluids. Other applications include the incorporation of such compositions, as is necessary, in disposable diapers, tampons, and 30 other personal hygiene products and applications.

The following examples are presented to further illustrate but not limit the scope of this invention. All parts and percentages are given based on weight, unless otherwise noted.

5 Example 1

A clear mixture of 1.05 grams (g) lauryl methacrylate in 12.5 g of a 30 percent solution of sodium lauryl sulfate is charged to a one-half liter jacketed reactor equipped with a stirrer, nitrogen sparge tube, gas outlet and thermometer. To the reactor is charged 270 g deionized water, 36 g acrylic acid, and 0.024 g of active 2,2'-azobis(2,4-dimethylpentane-nitrile) dissolved in 1 g polyethylene glycol of secondary alcohol surfactant. The reaction mixture is sparged with nitrogen. The reactor jacket is brought to 60°C and this temperature is maintained for 4 hours. The resulting gel is neutralized using 22.8 g of a 28.4 percent active aqueous ammonia solution. The neutralized gel is dried on a steam heated rotating drum apparatus. The resulting flake material is ground in a Waring Blender, Trademark of Dynamics Corporation of America, and screened such that particles having a size of less than 20 mesh (0.84 mm) are obtained.

The free swell capacity of the polymer (i.e., the grams of fluid absorbed per gram of polymer) is determined by dispersing 0.5 g of polymer in 150 g of a 1 percent aqueous sodium chloride solution, waiting 20 minutes, removing nonabsorbed water by pouring the mixture into a funnel lined with a 150 micron (150 nm) nylon screen, allowing free water to drain for 20 minutes, and weighing the drained (i.e., nonabsorbed) water. After drainage the gel is tough and firm indicating good gel strength. The free swell capacity of

the product is 54 gram of water absorbed per gram of polymer.

Example 2

5 A mixture of 1.05 g lauryl methacrylate in 6.25 g of a 60 percent solution of sodium dodecyl benzene sulfonate is charged into a reactor, as described in Example 1. To the reactor is charged 306 g deionized water, 36 g acrylic acid and 0.048 g of active catalyst dissolved in 1 g surfactant, as described in Example 1.

10 The mixture is subjected to polymerization conditions and isolated, as in Example 1. The free swell capacity of the product is 97 gram of water absorbed per gram of polymer, as determined as described in Example 1.

Example 3

15 A mixture of 0.75 g stearyl methacrylate in 6 g of a 30 percent solution of sodium lauryl sulfate is charged into a reactor, as described in Example 1. To the reactor is charged 315 g deionized water, 36 g acrylic acid and 0.024 g of active catalyst dissolved 20 in 1 g surfactant, as described in Example 1. The mixture is subjected to polymerization conditions and isolated, as in Example 1. The free swell capacity of the product is 91 gram of water absorbed per gram of polymer, as determined as described in Example 1.

25 Example 4

A mixture of 0.63 g lauryl methacrylate in 6.25 g of a 30 percent solution of sodium lauryl sulfate is charged into a reactor, as described in Example 1. To the reactor is charged 275 g deionized water, 36 g 30 acrylic acid and 0.038 g of active catalyst dissolved in 1 g surfactant, as described in Example 1. To the

mixture is added 15.4 g of alumina trihydrate. The mixture is subjected to polymerization conditions and isolated, as in Example 1. The free swell capacity of the product is 70 gram of water absorbed per gram of 5 polymer, as determined as described in Example 1.

Example 5

Into a citrate bottle is charged 96.6 parts acrylic acid (99.0 mole percent of monomers) as a 40 percent aqueous solution. The citrate bottle contains 10 10 parts sodium lauryl sulfate added as a 10 percent aqueous solution, 9.6 parts of a nonionic surfactant represented as $C_{12}H_{25}(EO)_5-H$, 6.4 parts of a nonionic surfactant represented as $C_{12}H_{25}(EO)_{10}-H$, and 3.4 parts (1.0 mole percent of monomers) lauryl methacrylate. The solution is stirred and 500 parts per million (ppm) based on total weight of the monomers of methylene-bis-acrylamide is added as an aqueous solution having a concentration of 1.25 percent in water. To this mixture is added 1,000 ppm based on monomer of an azobisisobutyronitrile catalyst as a 1.25 percent solution 15 in t-butyl alcohol. Distilled water is added to bring the monomer concentration of the mixture to 10 percent. The bottle is purged with nitrogen and the bottle is capped. The contents are subjected to polymerization 20 conditions at 60°C for 18 hours. The product is a thick gel which is drum dried and ground to 20 mesh (0.84 mm) particle size. The product is designated as Sample A. Gel capacity of this product is determined to be 70 g of absorbed 1 percent aqueous sodium 25 chloride solution per gram of product. Gel capacity is determined by contacting about 0.2 g of product with 25 g of said solution for about 20 minutes. The mixture is drained on a 20 mesh (0.84 mm) screen and 30 weighed.

5 Gel strength of this wet gel is determined to be 1.1 pounds per square inch (7.6 kPa). Gel strength is determined by placing weight on a piston placed over the gel until gel begins to extrude through the 20 mesh (0.84 mm) screen that the gel rests on.

10 For comparison purposes, an acrylic acid polymer crosslinked with 500 ppm methylene-bis-acrylamide yields a slimy product upon contact with the sodium chloride solution, and exhibits a gel strength of less than 0.4 pounds per square inch (2.8 kPa).

Example 6

15 A product is prepared and evaluated as described in Example 5, except that the recipe includes 1,000 ppm methylene-bis-acrylamide rather than 500 ppm. The product is designated Sample B. The gel capacity of the product is 45 g of absorbed 1 percent aqueous sodium chloride solution per gram of product. The gel strength of the product is 1.1 pounds per square inch (7.6 kPa), determined as described in Example 5.

20 For comparison purposes, an acrylic acid polymer crosslinked with 1,000 ppm methylene-bis-acrylamide yields a slimy product upon contact with the 1 percent sodium chloride solution, and exhibits a gel strength of less than 0.4 pounds per square inch (2.8 kPa).

25 Example 7

30 To each of 0.2 g of product Samples A and B from Examples 5 and 6 are added 2.5 g of a 2 percent dispersion of colloidal silica in a 1 percent aqueous sodium chloride solution. The product and dispersion are mixed, and to the mixture is added a few drops of ammonium hydroxide solution. Gel capacity of the sample

is determined as described in Example 5, and is determined to be 75 g of absorbed 1 percent aqueous sodium chloride solution per gram of polymer for Sample A mixed with the colloidal silica. The gel strength 5 of Sample A mixed with the colloidal silica is 2.75 pounds per square inch (19.0 kPa). Gel capacity is determined to be 80 g of absorbed 1 percent aqueous sodium chloride solution per gram of polymer for Sample B mixed with the colloidal silica. The 10 gel strength of Sample B mixed with the colloidal silica is 3.75 pounds per square inch (25.9 kPa).

1. A composition capable of absorbing an aqueous liquid which composition comprises a functionally effective amount of a swellable addition polymer comprising, in polymerized form, (a) a major portion of at least one water-soluble monomer, (b) a minor portion of at least one water-insoluble monomer having a pendant hydrophobic moiety, and optionally, (c) a minor portion of a crosslinking moiety in an amount sufficient to provide gel strength to the polymer; which polymer is polymerized in the presence of at least a micelle forming amount of a surfactant composition containing at least one ionic surfactant; and which polymer is capable of undergoing hydrophobic association through hydrophobic groups of said polymer such that said polymer is swellable but not readily soluble in the presence of an aqueous liquid when said polymer is in intimate contact with an amount of surfactant, if any, which is less than that amount of surfactant which will solubilize said polymer in said aqueous liquid.

2. The composition of Claim 1 wherein said polymer comprises, in polymerized form, from 90 to 99.995 mole percent of at least one water-soluble monomer, and from 0.005 to 10 mole percent of at least one monomer having a pendent hydrophobic moiety.

3. The composition of Claim 1 wherein said polymer additionally comprises, in polymerized form, from 0 to 50,000 ppm of crosslinkable monomer.

4. The composition of Claim 3 wherein said crosslinkable monomer is a polyvinyl monomer.

5. A composition of Claim 1 wherein said monomer having a pendant hydrophobic moiety is derived from the reaction of alkanols having from 4 to 20 carbon atoms with an ethylenically unsaturated carboxylic acid.

6. A composition of Claim 1 wherein said monomer having a pendant hydrophobic moiety is an alkyl acrylate or alkyl methacrylate wherein alkyl has from 4 to 20 carbon atoms.

7. The composition of Claim 1 containing a functionally effective amount of an inorganic colloidal support.

8. The composition of Claim 7 comprising from 20 to 100 weight percent polymer and from 0 to 80 weight percent colloidal support, based on the weight of the polymer and colloidal support.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US85/01533

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)³

According to International Patent Classification (IPC) or to both National Classification and IPC
 INT. CL⁷ C08L 31/02
 U.S. CL. 521/149

II. FIELDS SEARCHED

Minimum Documentation Searched⁴

Classification System	Classification Symbols
U.S.	521/149; 524/560, 561; 526/317; 604/368, 378

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched⁵

III. DOCUMENTS CONSIDERED TO BE RELEVANT¹⁴

Category ⁶	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	US, A, 4,293,609 PUBLISHED 06 OCTOBER 1981 ERICKSON	1-8
X	US, A, 4,066,583 PUBLISHED 03 JANUARY 1978 SPAULDING	1-8
X	US, A, 4,062,817 PUBLISHED 13 DECEMBER 1977 WESTERMAN	1-8
X	US, A, 3,926,891 PUBLISHED 16 DECEMBER 1975 GROSS ET AL	1-8
X	US, A, 4,190,562 PUBLISHED 26 FEBRUARY 1980 WESTERMAN	1-8
X	US, A, 4,432,881 PUBLISHED 21 FEBRUARY 1984 EVANI	1-8
X	US, A, 4,304,902 PUBLISHED 08 DECEMBER 1981 LANDOLL	1-8

* Special categories of cited documents:¹⁵

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search⁸

09 SEPTEMBER 1985

Date of Mailing of this International Search Report⁹

20 SEP 1985

International Searching Authority¹⁰

ISA/US

Signature of Authorized Officer¹⁰

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